CURVATURE OF THE WEINHOLD METRIC FOR THERMODYNAMICAL SYSTEMS WITH 2 DEGREES OF FREEDOM

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ABSTRACT. In this work [1] the curvature of Weinhold (thermodynamical) metric is studied in the case of systems with two thermodynamical degrees of freedom. Conditions for the Gauss curvature R to be zero, positive or negative are worked out. Signature change of the Weinhold metric and the corresponding singular behavior of the curvature at the phase boundaries are studied. Cases of systems with the constant C_v, including Ideal and Van der Waals gases, and that of Berthelot gas are discussed in detail.

1. INTRODUCTION

Usage of geometrical methods in homogeneous Thermodynamics started in the works by J.Gibbs ([7]) and C.Caratheodory ([6]) was further developed in the works of R.Hermann, R.Mrugala, in the dissertation of H.Heemeyer ([8]) and in other works. Thermodynamical metrics also have their source in the works of J. Gibbs ([7]). Explicitly a thermodynamical metric (TD-metric) was introduced by F.Weinhold ([33]) and, later, from a different point of view, by G.Ruppeiner ([29]). Deeper studies by P.Salamon and his collaborators, by P.Mrugala and H.Janyszek (see [3, 10, 11, 12, 13, 19, 20, 21, 23, 32]) clarified principal properties of thermodynamical metrics, relations between different TD-metrics and their place in relation to the contact structure of equilibrium thermodynamical phase space ([9, 18]). G. Ruppeiner (see review [30] and the bibliography cited there) has developed a covariant thermodynamical fluctuation theory based on the Riemannian metric η_S defined by the second momenta of entropy with respect to the fluctuations and related the curvature of this metric to the correlational volume near the critical point. He applied this scheme to a variety of models: ideal gas, ideal paramagnetic, Ising model, Takahashi gas, Van der Waals

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gas. P.Mrugala, H. Janyszek, P.Salamon studied the role of thermodynamical metrics in the statistical thermodynamics, one of examples being the model magnetic system ([13]).

These and some other developments, including an interest to thermodynamical metrics in the study of black holes led us to the question of a more systematic study of the curvature of thermodynamical metrics in the case of systems of smallest dimension where such curvature is present - the case where the phase space of TD-system is one with variables $(U; (T, S), (p, V), (\mu, N))$. Degeneracy of a TD metric η due to the homogeneity of a constitutive law (see [32] or see below) is removed by considering 1 mole of the media (or by the reduction procedure, [27]). As a result, a TD-metric is defined on the 2D constitutive surface (containing all equilibria states of the system). All the intrinsic curvature properties of this metric are defined by the scalar (Gauss) curvature R.

In Section 2 we introduce the thermodynamical metrics η_E defined by a thermodynamical potential E on the corresponding "constitutive surfaces" in the phase space of a thermodynamical system endowed with the contact structure ([5, 9]).

In Section 3 we introduce the elementary thermodynamical system (of two TD degrees of freedom) and calculate its Weinhold and Ruppeiner metrics. In addition we present examples of TD-metrics of a chemical system and the systems with magnetic and electrical properties.

In section 4 we calculate Levi-Civita connection and the curvature tensor of the metric η_E in the general n-dim case(see also [31]). In section 5 we introduce and study the Hessian surface H_E of the TD potential E in the space of symmetrical 2×2 matrices and express the curvature properties of the metric η_E in terms of geometrical properties of this surface. In particular, we determine the condition for the positivity, negativity and nullity of the scalar curvature $R(\eta_E)$ in terms of this surface.

In section 6 we continue the study in of curvature started in section 4 by calculating the determinant $det(\eta_E)$ (characterizing the signature of the metric) and the scalar curvature of the Weinhold metric η_U (defined by the internal energy U) of an elementary thermodynamical system in terms of T, V, heat capacity C_v, volume coefficient of expansion α, isothermal compressibility k and their derivatives.

In Sec.7 we consider the case of **constant** C_v where calculations simplify greatly. We define the form of the fundamental constitutive relations $U = U(S, V)$ in such a case and determine the systems of this type for which $R(\eta) = 0$ and the regions where scalar curvature is positive or negative.

In Sec.8, example of the ideal gas is considered. In Sec.9, we study the Weinhold metric for the Van der Waals gas, curve of the signature change (degeneracy curve of the $det(\eta)$), separating the domain of (stable) equilibria from the unstable region, scalar curvature behavior near this curve, calculation of critical values of physical variables in terms of the degeneracy curve. In Sec.11 the case of Berthelot gas is considered.

In the last Section 12 the geodesic equations of the Weinhold metric η_U for the general elementary thermodynamical system are obtained.

2. Weinhold Metric of a thermodynamical system

In this section we introduce, following [3, 9, 18, 21], some geometrical structure of on the (energy-phase) state space of homogenous thermodynamics and, in particular, the thermodynamical metrics ([33]) on the constitutive surfaces of this system - the principal object of our study.

We introduce the **thermodynamical phase space** P of a thermodynamical system with k "thermodynamical degrees of freedom" as a $(2k + 1)$-dimensional manifold endowed with a contact structure - 2D-distribution D on P which is totally non-integrable, [2]. This structure is presented (locally, and in many cases globally) by a contact (Pfaff) form ω such that $\omega \wedge (d\omega)^k \neq 0$ at each point of P.

The fundamental geometrical structure of a thermodynamical system is a choice of a canonical chart (Darboux chart) $\mathcal{C}$ of variables $z = (E, x^i, y_i, i = 1, \ldots k)$ for the 1-form ω, realizing it in the form

$$\omega = dE - \sum_{i=1}^{k} y_i dx^i. \tag{2.1}$$

Couples of variables (x^i, y_i) have the meaning of **extensive** (x^i) and **intensive** (y_i) variables, corresponding to the different processes that may undergo in the system and E is the chosen thermodynamical potential (internal energy, entropy, Helmholtz

free energy or entalpy, see [5]). Examples of couples (x^i, y_i) are: 1) temperature and entropy (T, S); 2) pressure and volume $(-p, V)$; 3) mole number of i-th component and corresponding electrochemical potential (N_i, μ_i); etc.

Horizontal distribution D of contact structure - subbundle of the tangent bundle $T(P)$

$$D_z = Ker(\omega(z)), \ z \in P \tag{2.2}$$

is endowed with the symplectic form $d\omega$ having, in a canonical chart $\mathcal{C}$, the standard form

$$d\omega = \sum_{i=1}^{k} dy^i \wedge dx^i \tag{2.3}$$

Admissible processes described by the system are **horizontal** curves $\gamma : t \to z(t) \in P$ of structure ω (i.e. such that $\gamma'(t) \in D_{\gamma(t)}$ for all t). In the case where E is interpreted as the internal energy of the system, $\int_\gamma dE$ is the work applied (or produced) during the process $\gamma(t)$, see ([5, 16]), and condition of admissibility ensures the fulfillment of the energy conservation law during the process.

Constitutive surfaces are defined as maximal integral surfaces of structure ω (Legendre submanifolds), ([2, 18]). Standard way to present such a surface Σ_E is to define it as the first jet of a function $E = E(x^i, i \in I; y_j, j \in [1, \ldots, k] \backslash I)$, defined in the open subset $D \subset R^k$. Here we choose a subset $I \subset [1, \ldots, k]$ of indices and take E to be a function of x^i with $i \in I$ and of y_j with j in the complemental set of indices $j \in [1, \ldots, k] \backslash I$. Relation $E = E(x^i, y_j)$ defines the fundamental constitutive relation of TD system, (see [5]), from which all others equations of state follows ([5]). In the usually considered case where $I = [1, \ldots, k]$ corresponding constitutive surface is given by

$$\Sigma_E = \{(E, x^i, y_j, i = 1, \ldots k) \in P | E = E(x^i), y_i = \frac{\partial E}{\partial x^i}, i \in [1, \ldots, k], (x^i) \in D \subset R^k\}. \tag{2.4}$$

From now on we will denote arguments of a function E defining a fundamental constitutive relation and the corresponding equilibria surface by $x^i, \ i \in [1, \ldots k]$.

Remark 1. Constitutive surface Σ_E defined by a function $E(x^i)$ contains the subsets $\mathcal{E}q_C \subset \Sigma_E$ of **equilibria states** of the homogeneous thermodynamical system

$E = E(x^i)$ subject to the (possible) constraints imposed on the system in the situation C (see [5] or other standard text in the thermodynamics for a variety of such situations). Subset $\mathcal{E}q_C \subset \Sigma_E$ is determined, due to the second law of thermodynamics, by the condition of extremum of the thermodynamical potential E subject to the constraints C, see [5, 16]. Submanifold Σ_E contains also unstable states as well as *locally stable* states ([5]). Partition of the constitutive surface Σ_E corresponding to a given family of constraints was studied in many cases (see [17, 5]). Geometry of the constitutive surface Σ_E, of its equilibria region(s) $\mathcal{E}q_C$ in relation to the admissible thermodynamical processes is one of the primary object of study of "geometrical thermodynamics", see [17, 18, 20, 21]).

Thermodynamical metric (TD-metric) defined by the constitutive relation $E = E(x^i)$ on the constitutive surface Σ_E of the contact structure ω has the form

$$\eta_E = \sum_{ij} \frac{\partial^2 E}{\partial x^i \partial x^j} dx^i \otimes dx^j. \tag{2.5}$$

For the case where E is the internal energy U, metric η_U is called the Weinhold metric. For the case where E is the entropy S, instead, metric η_S is called the Ruppeiner metric.

Notice that this form of the metric is not invariant under the diffeomorphisms of domain D (except linear ones, see [3] for more). Thus, though is not a drawback, TD-metric is defined by a physically meaningful choice of canonical chart $\mathcal{C}$ and transformation of this metric under the transition from one physically meaningful canonical chart to another one cannot be simple. As an example, we mention that the Legendre transformation of the space P leading to the replacement of internal energy U by the entropy S applied to the TD-metric η_U gives, as is shown in [20, 32], the TD-metric, conformal to the metric η_S on the equilibria surface X_U,

$$\eta_U = -\frac{1}{T}\eta_S.$$

Metric η_E with $E = U$ being the **internal energy** of a thermodynamical system, was introduced by F.Weinhold in series of papers [33]. It was further studied by P.Salaman, S.Berry and their collaborators (see [3, 23] and the bibliography in [28]).

Remark 2. A TD-metric η_E is induced on the surface Σ_E of the form (2.1) by the following symmetrical tensor

$$\tilde{\eta} = \frac{1}{2} \sum_{i=1}^{k} (dy_i \otimes dx^i + dx^i \otimes dy^i). \qquad (2.6)$$

This tensor is the only (up to a conformal factor) symmetrical tensor in P, annihilating the Reeb vector field Y of structure ω (here $Y = \frac{\partial}{\partial E}$), invariant under the substitution of indices i, and obtained as the sum of symmetrical tensors in the 2D-elementary subspaces D_i^* of D_x^* spanned by couples of covectors (dx^i, dy_i) of thermodynamically conjugated variables.

A very interesting way to construct all the TD-metrics η_E in the framework of the contact geometry was suggested by R.Mrugala ([19]). He has defined (starting from some arguments of statistical mechanics) the contact metric G on the phase space P inducing TD metric (2.5) on each equilibria surfaces. Geometrical properties of this metric are studied in the forthcoming work of the second author with J.Vargo [28] .

Function E defining constitutive relation and the constitutive surface Σ_E is assumed to be homogeneous of the first order: $E(\lambda x^i) = \lambda E(x^1)$,[5]. As a result, Weinhold metric is degenerate - its kernel is generated by the radial vector field in the space X

$$Ker(\eta) = R \cdot (x^i \frac{\partial}{\partial x^i})$$

This can be remedied either restricting all considerations to the subspace of X (and the section of cone Σ_E) with fixed value of one of variables x^i (mole number or volume are typical examples, see [23]) or using the geometrical reduction of the surface σ_E by the action of this dilatation group ([27]).

After this reduction of the TD-system its Weinhold metric is in general non-definite - the constitutive surface Σ_E is the union of domains of where this metric has different signature separated by the submanifolds (generically of codimension one) of states where this metric is degenerate. Submanifold of thermodynamical equilibria in the processes with a given set of constrains C - $\mathcal{E}q_C$ of the constitutive surface Σ_E lays the region of the **definite TD-metric** due to the second law of thermodynamics which requires the entropy to be (locally) maximal and energy to be (locally) minimal in the stable equilibria state to which system tends.

Gauss curvature R of thermodynamical metrics (in energy or entropy form) was calculated for several TD systems with two degrees of freedom (i.e. 5-dim phase space P) - ideal gas ($R = 0$), Takahashi gas, multi-component ideal gas, paramagnetic ideal gas, Van-der-Waals gas, ideal quantum gases(see review [29]). G. Ruppeiner (see review [30] and the bibliography cited there) related the curvature $R(\eta_S)$ of the metric defined by entropy to the correlational volume near the critical point. The fact that for the ideal gas the curvature of Weinhold metric η_U and that of Ruppeiner metric η_S is zero and the calculations of curvature for systems mentioned above allows to suggest some relation between this curvature (or at least its sign or nullity) and the interactions undergoing in the system on the microscopic level. Clarification of these questions requires deeper study of intrinsic and especially extrinsic geometry of constitutive submanifolds Σ_E of the thermodynamical phase space P.

3. Elementary TD system and other examples

Here we present several examples of TD-metrics including the basic **elementary thermodynamical system** with 5-dim phase space P in variables (U, S, T, p, V).

3.1. **Elementary TD-system.** As the first example of a thermodynamical system and its Weinhold and Ruppeiner metrics we consider the system with 5-dimensional phase-energy space of variables $(U, (S, T), (V, -p))$ which we will call from now on an **elementary thermodynamical system**. This system will be the principal object of our study here, so we will consider it in more details. Contact form ω of such a system can be chosen in a form

$$\omega = dU - TdS + pdV. \tag{3.1}$$

Consider a 2D integral submanifold Σ_U of this system defined by a constitutive relation

$$U = U(S, V), \tag{3.2}$$

with S and V being our extensive variables, T and p the relative conjugate intensities and U the internal energy function of the extensive variables.

Then

$$dU = (\frac{\partial U}{\partial S})dS + (\frac{\partial U}{\partial V})dV = TdS - pdV. \tag{3.3}$$

Notice that homogeneity condition for any constitutive relation in U-system ([5]) leads to the relation

$$U = ST - pV, \tag{3.4}$$

that should be fulfilled for all integral surfaces of contact structure ω given by a constitutive equation. Correspondingly, contact condition for thermodynamical processes has two forms, i.e.

$$\omega = dU - TdS + pdV = SdT - Vdp = 0$$

where the second one (Gibbs-Duhem equation, see [5]) leads to the second form of constitutive relation provided the constitutive relation in the first (fundamental) form is chosen.

Calculating the Weinhold metric of U-system we will use some notations standard in the literature (see [5]). Namely, we denote

(1) C_v is the heat capacity at constant volume:

$$C_v = T(\frac{\partial S}{\partial T})_V, \tag{3.5}$$

(2) C_p is the heat capacity at constant pressure:

$$C_p = T(\frac{\partial S}{\partial T})_p, \tag{3.6}$$

(3) α is the volume coefficient of expansion:

$$\alpha = \frac{1}{V}(\frac{\partial V}{\partial T})_p \tag{3.7}$$

(4) k is the isothermal compressibility:

$$k = -\frac{1}{V}(\frac{\partial V}{\partial p})_T \tag{3.8}$$

These quantities are related by:

$$C_p - C_v = VT\frac{\alpha^2}{k} \tag{3.9}$$

Calculating Weinhold metric for U-system on the two-dimensional integral surface $\Sigma_U(S, V)$ and using introduced notations we get

$$\eta_U = (\eta_{ij}) = \frac{1}{C_v} \begin{pmatrix} T & -\frac{T\alpha}{k} \\ -\frac{T\alpha}{k} & \frac{C_p}{vk} \end{pmatrix} \tag{3.10}$$

Characteristic equation of tensor η_{ij} (with respect to the canonical Euclidian metric h on the (S, V)-plane) is

$$\lambda^2 - (\frac{T}{C_v} + \frac{C_p}{C_v V k})\lambda + \frac{T}{C_v V k} = 0, \tag{3.11}$$

and

$$\lambda_\pm = \frac{1}{2}[(\frac{T}{C_v} + \frac{C_p}{C_v V k}) \pm \sqrt{\triangle}]$$

For the discriminant $\triangle$ we have the following inequality

$$\triangle = (\eta_{11} - \eta_{22})^2 + (2\eta_{12})^2 = (\frac{T}{C_v} - (\frac{C_p}{C_v V k}))^2 + (2\frac{T\alpha}{C_v k})^2 > 0 \tag{3.12}$$

which, in particular, implies that

$$\det_h \eta_{ij} < \frac{1}{4}(trace_h(\eta_{ij}))^2 \tag{3.13}$$

Remark 3. Notice that since $C_p = C_v + \frac{VT\alpha^2}{k}$, discriminant $\triangle$ is always positive. Therefore eigenvalues $\lambda_\pm$ are both real and distinct.

Moreover, since $\det \eta_{ij} = \lambda_+ \lambda_-$, and since also $\det \eta_{ij} = -\frac{T}{C_v}(\frac{\partial p}{\partial V})_T$, we get the following

Lemma 1. *Let $T > 0$. Then*
  1) *If $C_v > 0$ and $(\frac{\partial p}{\partial V})_T < 0$ then $\det \eta_{ij} > 0$ and $\lambda_\pm > 0$.*
  2) *If $C_v < 0$ and $(\frac{\partial p}{\partial V})_T > 0$ then $\det \eta_{ij} > 0$ and $\lambda_\pm < 0$.*
  3) *If C_v and $(\frac{\partial p}{\partial V})_T$ have different sign then $\det \eta_{ij} < 0$ and $\lambda_+ > 0$, $\lambda_- < 0$.*

Fulfillment of 1) and 2) guarantees the stability for the system even if the case 2) might look non physical at all. However, there are some cases when it is natural to assume that the heat capacity is negative (in a cluster of sodium atoms or in the black holes, [24]). There are also cases in which the isothermal (and adiabatic) compressibility seems to be negative (in amino acid, [22]). These are examples of cases away from stability.

Example 1. In case of an Ideal Gas, $\alpha = \frac{1}{T}$ and $k = \frac{1}{p}$, and the metric η_U is given by

$$\eta_{Uij} = \frac{1}{C_v}\begin{pmatrix} T & -p \\ -p & \frac{C_p p}{v} \end{pmatrix} \tag{3.14}$$

Applying Legendre's transformation from variables $(U, (S, T), (V, -p))$ to the variables $(S, (U, T^{-1}), (V, pT^{-1}))$ to the contact form ω and rewriting the constitutive relation correspondingly, we get

$$\omega = dU - TdS + pdV = -T\left[dS - \frac{1}{T}dU - \frac{p}{T}dV\right] = 0 \Rightarrow \omega = dS - \frac{1}{T}dU - \frac{p}{T}dV, \tag{3.15}$$

and

$$S = S(U, V) \tag{3.16}$$

Correspondingly, TD-metric on the two-dimensional integral surface $\Sigma_S(U, V)$ (Ruppeiner metric) takes the form, see also [19],

$$\eta_{Sij} = \begin{pmatrix} -\frac{1}{C_v T^2} & \frac{1}{T^2}\left(\frac{T\alpha - kp}{kC_v}\right) \\ \frac{1}{T^2}\left(\frac{T\alpha - kp}{kC_v}\right) & -\frac{1}{C_v}\left(\frac{T\alpha - kp}{Tk}\right)^2 - \frac{1}{VkT} \end{pmatrix} \tag{3.17}$$

In case of an Ideal Gas, metric (3.17) takes the form

$$\eta_{Sij} = \begin{pmatrix} -\frac{1}{C_v T^2} & 0 \\ 0 & -\frac{p}{VT} \end{pmatrix} \tag{3.18}$$

due to the Gibbs-Duhem form of constitutive relation $(T\alpha - kp) = 0$.

3.2. **A chemical system.** Here we consider a $(2m+5)$ homogeneous thermodynamical system in energy-phase space defined by

$$(S, (U, \frac{1}{T}), (V, \frac{p}{T}), (N_1, \frac{\mu_1}{T}), ...(N_m, \frac{\mu_m}{T})) \tag{3.19}$$

with N_i being the number of molecules of type i and μ_i being their conjugate intensities - chemical potential per molecule i-th.

Consider (m+2)-dim integral surface defined by an entropy constitutive relation

$$S = S(U, V, N_1, ...N_m) \tag{3.20}$$

We get

$$dS = \left(\frac{\partial S}{\partial U}\right) dE + \left(\frac{\partial S}{\partial V}\right) dV + \sum_i \left(\frac{\partial S}{\partial N_i}\right) dN_i$$

$$= \frac{1}{T} dU + \frac{p}{T} dV + \sum_i \frac{\mu_i}{T} dN_i. \tag{3.21}$$

Then we calculate

$$\eta_{Sij} = \begin{pmatrix} -\frac{1}{C_v T^2} & \frac{1}{T^2}\left(\frac{T\alpha - kp}{kC_v}\right) & \frac{\partial}{\partial E}\left(\frac{\mu_j}{T}\right) \\ \frac{1}{T^2}\left(\frac{T\alpha - kp}{kC_v}\right) & -\frac{1}{C_v}\left(\frac{T\alpha - kp}{Tk}\right)^2 - \frac{1}{VkT} & \frac{\partial}{\partial V}\left(\frac{\mu_j}{T}\right) \\ \frac{\partial}{\partial N_i}\left(\frac{1}{T}\right) & \frac{\partial}{\partial N_i}\left(\frac{p}{T}\right) & \frac{\partial}{\partial N_i}\left(\frac{\mu_j}{T}\right). \end{pmatrix} \tag{3.22}$$

3.3. Thermodynamical system in homogeneous Magnetic and Electric Fields.

Constitutive relation should now include the work of magnetic and electric field on the (homogeneous) system. Let's consider the work of magnetic field first. Fundamental result of the thermodynamics of magnetic system defines the differential of the magnetic work to be ([5]):

$$dW_{Magn} = d(\frac{\mu_0}{8\pi} \int H^2 dV) + \mu_0 \int (H \cdot dM) dV, \tag{3.23}$$

where H is the external magnetic field, M is the magnetization (magnetic momentum) vector. First term represents the change of energy of the magnetic field, second, the work of the magnetic field on the magnetic momentum of the system. Since we consider here only homogeneous systems, we take H to be constant. Let also assume that the magnetization M is homogeneous.

Then

$$dW_{Magn} = d(\frac{\mu_0}{8\pi} \int H^2 dV) + \mu_0 H \cdot dI \tag{3.24}$$

where $I^{tot} = \int M dV = MV$ is the total magnetic dipole moment of the system.

Considering just the contribution to the magnetic work due to the magnetic dipole moment I, let's define the (internal) energy to be

$$U = U(S, V, I_H^{tot}, N_1, N_2, ..., N_m), \tag{3.25}$$

where I_H^{tot} is the component of the total magnetic moment parallel to the external field. Then

$$dU = (\frac{\partial U}{\partial S})dS + (\frac{\partial U}{\partial V})dV + \sum_i (\frac{\partial U}{\partial N_i})dN_i + (\frac{\partial U}{\partial I_H^{tot}})dI_H^{tot}$$

$$= TdS - pdV + \sum_i \mu_i dN_i + \mu_0 H dI_H^{tot} \tag{3.26}$$

where μ_0 is the permittivity of free space.

Then the Weinhold metric for the system with constitutive relation (3.26) in the space of variables $(S, V, I_H^{tot}, N_1, N_2, ..., N_m)$ is

$$\eta_{Uij} = \begin{pmatrix} \frac{T}{C_v} & -\frac{T\alpha}{C_v k} & \frac{\partial T}{\partial I_H^{tot}} & \frac{\partial T}{\partial N_i} \\ -\frac{T\alpha}{C_v k} & \frac{C_P}{vC_v k} & -\frac{\partial p}{\partial I_H^{tot}} & -\frac{\partial p}{\partial N_j} \\ \mu_0 \frac{\partial H}{\partial S} & \mu_0 \frac{\partial H}{\partial V} & \mu_0 \frac{\partial H}{\partial I_H^{tot}} & \mu_0 \frac{\partial H}{\partial N_j} \\ \frac{\partial \mu_i}{\partial S} & \frac{\partial \mu_i}{\partial V} & \frac{\partial \mu_i}{\partial I_H^{tot}} & \frac{\partial \mu_i}{\partial N_J} \end{pmatrix} \tag{3.27}$$

Similarly, for the work of a homogeneous external electrical field E_l in homogeneous case we have ([5])

$$dW_{electr.} = d(\frac{\epsilon_0}{8\pi} \int E_l^2 dV) + E_l dP^{tot} \tag{3.28}$$

where $P^{tot} = PV$ is the total electric dipole moment.

Similarly to the previous case, if we consider just the contribution to the electric work due to the electric dipole moment, we can define the internal energy as follows

$$U = U(S, V, P_E^{tot}, N_1, ... N_m) \tag{3.29}$$

Then

$$dU = TdS - pdV + E_l dP_E^{tot} + \sum_i (\mu_i dN_i) \tag{3.30}$$

where

$$E_l = \frac{\partial U}{\partial P_E^{tot}}$$

P_E^{tot} is the component of the electric moment parallel to the external field.

Thus, the system consisting of several chemical components in the presence of an electrical filed takes the form

$$\eta_{Uij} = \begin{pmatrix} \frac{T}{C_v} & -\frac{p}{C_v} & \frac{\partial T}{\partial P_E^{tot}} & \frac{\partial T}{\partial N_j} \\ -\frac{p}{C_v} & \frac{pC_p}{vC_v} & -\frac{\partial p}{\partial P_E} & -\frac{\partial p}{\partial N_j} \\ \frac{\partial E_l}{\partial S} & \frac{\partial E_l}{\partial V} & \frac{\partial E}{\partial P_E^{tot}} & \frac{\partial E}{\partial N_j} \\ \frac{\partial \mu_i}{\partial S} & \frac{\partial \mu_i}{\partial V} & \frac{\partial \mu_i}{\partial P_E^{tot}} & \frac{\partial \mu_i}{\partial N_j} \end{pmatrix} \tag{3.31}$$

4. CURVATURE OF TD-METRIC OF A GENERAL THERMODYNAMICAL SYSTEM

In this section, we consider a thermodynamical potential $E = E(x_i)$ as function of the extensive variables x_i and calculate the curvature of the corresponding thermodynamical metric defined on the integral (constitutive) surface Σ_E, by the equation (2.3)

$$\eta_{Eij} = \frac{\partial^2 E}{\partial x_i \partial x_j}.$$

Christoffel symbols for this metric are given by

$$\Gamma_{ij}^k = \frac{1}{2} \sum_m \eta_{ij,m} \eta^{km}, \tag{4.1}$$

where $\eta_{ij,m} = \frac{\partial \eta_{ij}}{\partial x^m}$.

After some calculations, it can be shown that the curvature tensor of metric η_E is given by

$$R_{ijk}^l = \Gamma_{ki,j}^l - \Gamma_{ji,k}^l + \Gamma_{jp}^l \Gamma_{ki}^p - \Gamma_{kp}^l \Gamma_{ji}^p = \frac{1}{4}(\eta_{ij,m}\eta_{sn,k} - \eta_{sn,j}\eta_{ki,m})\eta^{mn}\eta^{ls} \tag{4.2}$$

Therefore, Ricci Tensor of metric η_E is

$$R_{ik} = R_{ijk}^j = \frac{1}{4}(\eta_{ij,m}\eta_{sn,k} - \eta_{sn,j}\eta_{ki,m})\eta^{mn}\eta^{js}, \tag{4.3}$$

and its scalar curvature $R(\eta)$ is, see also [31],

$$R = R_{ik}\eta^{ik} = \frac{1}{4}(\eta_{ij,m}\eta_{sn,k} - \eta_{sn,j}\eta_{ki,m})\eta^{mn}\eta^{js}\eta^{ik}. \tag{4.4}$$

5. Hessian Surface of a thermodynamical potential and the sign of scalar curvature $R(\eta_E)$

In this section we study the Hessian representation of a metric η_E of a 5-dim thermodynamical system with two "degrees of freedom" (using the terminology of Mechanics) x^i, $i = 1, 2$ in terms of an oriented 2D surface in 3D space of symmetrical 2×2 matrices. We find a geometrical conditions on this surface determining regions where scalar curvature of η_E is positive, negative, zero, singular. In later sections we demonstrate, on examples of ideal, van der Waals and Berthelot gases - to what physical consequences these properties of metric η_U lead to.

5.1. **Scalar curvature, 2D case.** For $k = 2$ and a metric $\eta = \begin{pmatrix} \eta_{11} & \eta_{12} \\ \eta_{21} & \eta_{22} \end{pmatrix}$, we can use the known formula for scalar curvature ([26], Ch.VIII, Sec.2)

$$R = -\frac{1}{4det(\eta)^2}det\begin{pmatrix} \eta_{11} & \eta_{11,1} & \eta_{11,2} \\ \eta_{12} & \eta_{12,1} & \eta_{12,2} \\ \eta_{22} & \eta_{22,1} & \eta_{22,2} \end{pmatrix} - \frac{1}{\sqrt{det(\eta)}}\left[\left(\frac{\eta_{11,2} - \eta_{12,1}}{\sqrt{det(\eta)}}\right)_{,2} - \left(\frac{\eta_{12,2} - \eta_{22,1}}{\sqrt{det(\eta)}}\right)_{,1}\right], \tag{5.1}$$

which, for the Weinhold metric reduces to the first term only:

$$R = -\frac{1}{4det(\eta)^2}det\begin{pmatrix} \eta_{11} & \eta_{11,1} & \eta_{11,2} \\ \eta_{12} & \eta_{12,1} & \eta_{12,2} \\ \eta_{22} & \eta_{22,1} & \eta_{22,2} \end{pmatrix}. \tag{5.2}$$

This expression shows that the scalar curvature goes to infinity as $det(\eta) \to 0$.

Remark 4. Notice that the condition on a function E that the metric η_E is **degenerate everywhere**, i.e.

$$det(\eta_E) = \eta_{11}\eta_{22} - \eta_{12}^2 = 0$$

is the simplest **Monge-Ampere equation**,[1]. Geometry on the surfaces defined by such a function is very interesting and well studied (see, for instance [1] and the bibliography therein) but has little relation to the case where E is a thermodynamical potential of a physically interesting system.

5.2. **Hessian surface of a function** E. Scalar curvature R is zero if and only if the determinant in the numerator of expression (5.2) is zero. To determine where it can take place, consider the **Hessian mapping** $Hess_E$ of a function E mapping a 2D (canonically oriented) domain D of variables x^1, x^2 into the 3D vector space of 2x2 symmetrical matrices $Sym(2, R)$ with the coordinates η_{ij}:

$$Hess_E : (x^1, x^2) \rightarrow \begin{pmatrix} E_{,11} & E_{,12} \\ E_{,12} & E_{,22} \end{pmatrix}. \tag{5.3}$$

Image of this mapping is the 2D oriented surface H_E in the vector space $Sym(2, R)$. This surface is endowed with the frame formed by the coordinate tangent vectors to this surface $\mathbf{r}_i(x) = Hess_{E *x}(\frac{\partial}{\partial x^i})$ at the nonsingular points of the surface where these vectors are linearly independent. This determines orientation of the surface H_E, or, what is the same, field of normal vectors $\mathbf{N} = \mathbf{r}_1(x^1, x^2) \times \mathbf{r}_2(x^1, x^2)$, where $\times$ is the standard vector product in R^3.

Notice that, given a function E, the physically relevant domain $D \subset R^2$ where mapping $Hess_E$ is defined can be smaller then the natural domain $D(E)$ of the function E. As an example, let us note the condition of **positivity** of some physical quantities (volume, pressure) or other lower boundary (Kelvin temperature) condition. Sometimes it is reasonable to assume that function E is defined on the boundary of domain D. Correspondingly, not all the surface H_E is interesting from the point of view of physics. Example of such a situation is given below.

Condition of degeneracy of a matrix defines in the space $Sym(2, R)$ the standard conic (nilpotent cone)

$$\eta_{11}\eta_{22} - \eta_{12}^2 = 0. \tag{5.4}$$

Subset of degeneracy $sing(\eta_E) \subset D$ of the metric η_E is the pre-image under the $Hess_E$ of the intersection of surface H_E and the cone (5.4).

Example 2. As the first example of the $Hess(E)$ consider the ideal gas whose internal energy U as a function of variables S, V and the mole number N has the form

$$U = U_0 + C_v N \left(\frac{V}{N}\right)^{-\frac{R}{C_v}} e^{\frac{1}{C_v}(\frac{S}{N} - S_0)},$$

see [16], Chapter 6. For one mole, taking $N = 1$ we find

$$\eta_U = \frac{R}{C_v} e^{\frac{S}{C_v}} \begin{pmatrix} \frac{1}{R} V^{-\frac{R}{C_v}} & -V^{-\frac{C_p}{C_v}} \\ -V^{-\frac{C_p}{C_v}} & C_p V^{-(1+\frac{C_p}{C_v})} \end{pmatrix}. \tag{5.5}$$

Excluding variables S, V from the formula for Weinhold metric, it is easy to get equation for the surface H_U

$$R\eta_{11}\eta_{22} - C_p \eta_{12}^2 = 0. \tag{5.6}$$

Thus the surface $\Sigma_U \subset Sym(2, R)$ is trivially isomorphic to the standard **conic** $xz - y^2 = 0$ in R^3. Conic (5.5) defines the homogeneous nonlinear second order (Monge-Ampere) PDE

$$RU_{,11}U_{,22} - C_p U_{,12}^2 = 0$$

satisfied by the energy function U of the ideal gas (see Theorem 2 below).

Comparing equations (5.4) and (5.6) we see that the signature degeneration may happen on the Hessian surface of ideal gas only in **nonphysical** points $\eta_{12} = \eta_{11}\eta_{22} = 0$ or under the condition $C_p = R$, i.e. when $C_v = 0$.

Example 3. As the second example, consider the van der Waals gas with molar internal energy (9.6) and the Weinhold metric (9.8). Excluding e^{S/C_v} and V from the equation (9.8) we get equation for the Hessian surface H_U for the vdW gas:

$$R\eta_{22}\eta_{11} - C_p \eta_{12}^2 = -\frac{2aR\eta_{11}\eta_{12}^3}{(b\eta_{12} - R\eta_{11})^3}. \tag{5.7}$$

Expression on the right is the (linear) correction to the ideal gas equation for the Hessian surface ensuring nonzero curvature almost everywhere on this surface. Multiplying by the denominator we get the algebraic equation for H_E

$$(b\eta_{12} - R\eta_{11})^3 (R\eta_{22}\eta_{11} - C_p \eta_{12}^2) + 2aR\eta_{11}\eta_{12}^3 = 0.$$

given by the **polynomial of the fifth order**.

Intersection of this surface with the surface $det(\eta_{ij}) = 0$ determines the curve of the signature change (critical curve) for the vdW gas (in this representation)

$$\eta_{12}[2aR\eta_{11}\eta_{12} - C_v(b\eta_{12} - R\eta_{11})^3] = 0$$

Remark 5. It is interesting to notice that in these two examples the Hessian surface H_E is turned to be **algebraic**. In general case of C_v-const (see the constitutive equation (7.3)) this is not so anymore.

5.3. **Zero curvature condition.** Equality of the determinant in the numerator of the formula for curvature to zero is equivalent to the linear dependency of radius vector $Hess_E(x)$ of a point of the surface and two tangent vectors $\mathbf{r}_i(x)$.

Endow the space $Sym(2, R)$ with the canonical metric

$$(A, B) = TR(AB),$$

induced by the Killing metric on the Lie algebra $sl(2, R)$, [14]. Choosing the orthonormal basis:

$$X_1 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad X_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad X_3 = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix},$$

allows to identify $Sym(2, R)$ with R^3

$$\begin{pmatrix} a & b \\ b & c \end{pmatrix} \longleftrightarrow \begin{pmatrix} a \\ \sqrt{2}b \\ c \end{pmatrix}$$

and to introduce scalar product with the standard Euclidian scalar product $<\ ,\ >$.

Then, the determinant in the numerator of formula (5.2) takes the form

$$2^{3/2} < Hess_E(x^1, x^2), \mathbf{N}(x^1, x^2) >, \tag{5.8}$$

where $\mathbf{N}$ is the normal vector to the surface H_E introduced above. Thus, we can use alternatively picture of surface H_E in $Sym(2, R)$ and the standard Euclidian R^3-representation of this surface and other objects. We will use standard cartesian coordinates (x, y, z) in R^3.

Let $\Phi(x, y, z) = 0$ be an equation of a surface Σ^2 in $R^3 \equiv Sym(2, R)$ satisfying, on some open set $D \subset \Sigma$ where the surface Σ is smooth (nonsingular), to the condition above: radius vector $\bar{r}$ at each point of the surface is parallel (and belongs) to the tangent plane of the surface at this point. This means, in particular, that tangent planes at each point of the surface pass through the origin. Since radius vector $\bar{r}$ at

the point of the surface $\Phi(x, y, z) = 0$ belongs to the tangent plane of the surface at that point, then

$$\frac{\partial}{\partial t}\Phi(\bar{r} + t\bar{r}) = 0$$

at each point of the domain D. From this it follows that

$$\bar{r} \cdot \nabla\Phi = 0$$

on the subset D of the surface $\Phi(x, y, z) = 0$. In other words, radial vector field $q = \bar{r} \cdot \nabla$ is tangent to the surface $\Phi(x, y, z) = 0$. Therefore, subset D of this surface is invariant under the (local) action of the group of dilations - phase flow of vector field q.

Thus, in an open subset D where $R = 0$, surface $H_E(D)$ is **conical** and vice versa.

Consider now the projectivization $P_2(R) = P(Sym(2, R))$ of the 3D vector space $Sym(2, R)$. Image of the conical surface $H_E(D)$ in this projective space is one-dimensional and, near nonsingular points (on an open subset of this image) is a smooth curve. In homogeneous coordinates (x, y, z) of $P(Sym(2, R))$, this curve is (locally) given by an equation

$$L(x, y, z) = 0, \tag{5.9}$$

with a **homogeneous function** L. This equation is also the equation of the surface $H_E(D) \subset Sym(2, R)$ near almost all points.

Vice versa, if a surface in $Sym(2, R)$ is given by a homogeneous equation of the type (5.5), it is conical.

As a result we see that components of Hessian of function U must satisfy to the following homogeneous (nonlinear in general) second order PDE

$$L(E_{x^1 x^1}, E_{x^1 x^2}, E_{x^2 x^2}) = 0. \tag{5.10}$$

These arguments prove the following:

Theorem 1. *Let $k = 2$, and let $E(x^1, x^2)$ be a smooth function. Following statements are equivalent*

(1) *Weinhold metric η_E has zero scalar curvature on an open subset $D \subset R^2$.*
(2) *Image of subset D under the Hessian mapping $Hess_E : R^2 \to Sym_2(2, R)$ is a **conical** surface.*

(3) *Function E satisfies to a* **homogeneous** *second order partial differential equation*

$$L(E_{x^1 x^1}, E_{x^1 x^2}, E_{x^2 x^2}) = 0$$

on the open set D.

Consider in more details the case where the conical surface H_E is a plane. This case has no, as far as we know, a direct physical application but is interesting as allowing to get the explicit necessary and sufficient condition on the thermodynamical potential E to have zero scalar curvature $R(\eta_E)$.

In this case there is a constant vector $\gamma \in Sym(2, R)$ such that radius vector $Hess_E(x)$ of the surface is orthogonal to γ at all points $(x^1, x^2) \in D$.

In these terms, condition of zero curvature above takes the form

$$\gamma_1 \eta_{11}(x) + \gamma_2 \eta_{12}(x) + \gamma_3 \eta_{22}(x) = 0$$

for all $x \in V$. Vector γ is defined up to a multiplication by a nonzero factor.

Last equation can be rewritten as the 2nd order linear PDE for the function $U(x^1, x^2)$:

$$LU = \left(\gamma_1 \frac{\partial^2}{\partial x^{1\,2}} + \gamma_2 \frac{\partial^2}{\partial x^1 x^2} + \gamma_3 \frac{\partial^2}{\partial x^{2\,2}} \right) U = 0. \tag{5.11}$$

Linear nondegenerate transformation in the plane (x^1, x^2) transforms linear differential operator of the second order with constant coefficients L to one of three canonical forms:

(1) If $\gamma_1 \gamma_3 - 1/4 \gamma_2^2 > 0$, to the (elliptic) form

$$\Delta = \frac{\partial^2}{\partial u^{1\,2}} + \frac{\partial^2}{\partial u^{2\,2}}.$$

(2) If $\gamma_1 \gamma_3 - 1/4 \gamma_2^2 = 0$, to the (degenerate) form

$$D = \frac{\partial^2}{\partial u^{1\,2}} + \frac{\partial^2}{\partial u^{2\,2}}.$$

(3) If $\gamma_1 \gamma_3 - 1/4 \gamma_2^2 < 0$, to the (hyperbolic) form

$$\square = \frac{\partial^2}{\partial u^{1\,2}} - \frac{\partial^2}{\partial u^{2\,2}}.$$

Correspondingly, solutions of equation (5.10) can be described as the composition of an arbitrary solution of one of these three model equations with a linear non-degenerate transformation in the plane (x^1, x^2).

This finishes the proof of the first part of the following theorem.

Theorem 2. *For a thermodynamical system with two degrees of freedom and a constitutive relation $E = E(x^1, x^2)$ the following statements are equivalent:*

(1) *Scalar curvature R of the (Weinhold) metric $\eta = \frac{\partial^2 E}{\partial x^i \partial x^j}$ equals zero in an open set $D \subset R^2$ and image of D under the Hessian mapping is the (part of) plane.*

(2) *Each point $z \in D$ has a neighborhood W such that the generating function $E(x^1, x^2)$ satisfies to an equation*

$$LE = \left(\gamma_1 \frac{\partial^2}{\partial x^{1\,2}} + \gamma_2 \frac{\partial^2}{\partial x^1 x^2} + \gamma_3 \frac{\partial^2}{\partial x^{2\,2}} \right) E = 0. \tag{5.12}$$

with some $\gamma \in R^3$ and

    (a) *(elliptic case) If $\gamma_1 \gamma_3 - 1/4 \gamma_2^2 > 0$, then E is the composition of a harmonic function on R^2 with a nondegenerate linear transformation of the plane (x^1, x^2).*

    (b) *(degenerate case) If $\gamma_1 \gamma_3 - 1/4 \gamma_2^2 = 0$, then E is the composition of an arbitrary function $f(x^1)$ of variable x^1 with a nondegenerate linear transformation of the plane (x^1, x^2).*

    (c) *(hyperbolic case) If $\gamma_1 \gamma_3 - 1/4 \gamma_2^2 < 0$, E is the composition of a function of the form $f(x^1 + x^2) + g(x^1 - x^2)$ with arbitrary functions f, g of one variable with a nondegenerate linear transformation of the plane (x^1, x^2).*

(3) *Statement of part two is valid in the whole open connected set D with the same vector γ.*

Proof. To prove the last statement of Theorem 2, notice that, unless surface H_E degenerates to a straight line, E cannot satisfy to two equations with nonparallel vectors γ^k. As a result, local statement of the theorem can be extended to the whole connected set D with the same vector γ. □

5.4. **Positive and negative scalar curvature - geometrical condition.** Generically, the set of points (x^1, x^2) where $R(\eta_E) = 0$ represent the curve (possibly singular i.e. consisting of isolated points) on the plane (x^1, x^2) - pre-image under the mapping

$Hess_E$ of the set - points that are singular for the mapping $H_E \to P(Sym(2, R))$ of projectivization.

If at some point (x^1, x^2), $R(x^1, x^2) \neq 0$, then the sign of $R(x^1, x^2)$ is invariant under the relabelling of variables x^1, namely, when we change $y^1 = x^2$, $y^2 = x^1$, in the expression (5.2) for curvature, denominator is not changing while the two last columns of the determinant of the matrix in the numerator are permuted. But at the same time, first and last rows of the matrix in the numerator are permuted too restoring the sign of the scalar curvature.

Definition 1. *Let Σ^2 be an oriented surface in $\mathbb{R}^3$. We call the surface Σ^2 (with the normal $\bar{N}$),* **radially convex** *(correspondingly,* **radially concave***)) if $\bar{r} \cdot \bar{N} > 0$ for all $\bar{r} \in \Sigma^2$ (correspondingly $\bar{r} \cdot \bar{N} < 0$ for all $\bar{r} \in \Sigma^2$).*

Then, as the arguments above shows, the following statement is true,

Theorem 3. *Let $V \subset H_E$ be an open subset of the surface H_E. Following statements are equivalent:*

(1) *$R > 0$ (correspondingly $R < 0$) for $\bar{r} \in V$,*
(2) *Surface $H_E|_V$ is radially convex (correspondingly radially concave).*

5.5. **Conformal equivalence of Weinhold and Ruppeiner metrics and the curvatures.** Recalling ([5, 18]) that thermodynamical metrics η_U and η_S are related by contact transformations, generated by the mapping ϕ of canonical "internal energy" chart $(U, (T, S), (-P, V), (\mu_i, N_i))$ to the entropy chart $(S, (-T^{-1}, U), (\frac{-p}{T}, V), (\frac{\mu_i}{T}, N_i))$. More specifically, we have, for the contact form in these two charts

$$\phi^* \omega_S = \tau \omega_U, \ \tau = T^{-1}, \tag{5.13}$$

Correspondingly, equilibrium surface Σ_U is mapped onto the corresponding surface Σ_S. For **metrics** η_U, η_S **on these surfaces** we have the following conformal equivalence relation ([32, 19]:

$$\phi^* \eta_S = \tau \eta_U, \ \tau = T^{-1}, \tag{5.14}$$

noticeably with the same conformal factor $\frac{1}{T}$ as the contact form ω.

Recall ([25], Ch.18) that if two metrics on a smooth manifold M are conformally equivalent:

$$\bar{g} = e^{2\sigma} g, \tag{5.15}$$

with some function $\sigma \in C^{\infty}(M)$, then, their scalar curvatures are related by

$$e^{2\sigma} R(\bar{g}) = R(g) - 2(n-1)S, \tag{5.16}$$

where n is the dimension of the manifold M and $S = g^{ik} S_{ik}$, with

$$S_{ij} = \nabla_j^g \sigma_i - \sigma_{,i}\sigma_{,j} + \frac{1}{2} g_{ij} g^{kl} \sigma_{,k}\sigma_{,l}.$$

Thus after conformal transformation one get in the expression for scalar curvature the additional term

$$S = g^{ij} S_{ij} = g^{ij}\nabla_j^g \sigma_i - g^{ij}\sigma_{,i}\sigma_{,j} + \frac{1}{2} g^{ij} g_{ij} g^{kl} \sigma_{,k}\sigma_{,l} = \nabla_j^g \sigma^j - \|d\sigma\|_g^2 + \frac{n}{2}\|d\sigma\|_g^2. \tag{5.17}$$

First term on the right in the last part of this formula is the covariant divergence with respect to the original metric g of the gradient (with respect to g) of function σ:

$$div_g(\nabla^g \sigma) = \Delta_g \sigma.$$

Thus,

$$S = \Delta_g \sigma + \frac{n-2}{2}\|d\sigma\|_g^2.$$

For $n = 2$, the second term vanishes and we get for scalar curvatures the following relation

$$e^{2\sigma} R(\bar{g}) = R(g) - 2(\Delta_g \sigma). \tag{5.18}$$

In our case above $\sigma = -\frac{1}{2} ln(T)$, so we get relation between curvatures of Ruppeiner η_S and Weinhold η_U (expressed in coordinates (S, V)):

$$R(\eta_S) = T R(\eta_U) + T \Delta_g ln(T). \tag{5.19}$$

It follows from this that scalar curvatures of both metrics are zero simultaneously if and only if the logarithm of temperature $ln(T)$ is the **harmonic function** of (S, V).

6. Curvature of a general 2-D elementary system

In this section we study the scalar curvature of a general 2-dim elementary thermodynamical system.

We found in Section 3 the Weinhold metric of any two-dimensional elementary system of entropy S and volume V to be, (3.14),([19]),:

$$\eta_U = (\eta_{Uij}) = \frac{1}{C_v} \begin{pmatrix} T & -\frac{T\alpha}{k} \\ -\frac{T\alpha}{k} & \frac{C_p}{vk} \end{pmatrix}$$

Determinant of the tensor η_U (with respect to the standard Euclidian metric) is

$$det(\eta_{Uij}) = \frac{TC_p}{VkC_v^2} - \frac{T^2\alpha^2}{k^2C_v^2} = \frac{T}{kC_v^2}(\frac{C_p}{V} - \frac{T\alpha^2}{k}) = \frac{T}{kC_v^2}(\frac{C_v}{V} + \frac{T\alpha^2}{k} - \frac{T\alpha^2}{k}) = \frac{T}{kVC_v} \tag{6.1}$$

Using definition of k as above, we finally get

$$det(\eta_{Uij}) = -\frac{T}{C_v}(\frac{\partial p}{\partial V})_T \tag{6.2}$$

Excluding T from being zero, the metric η_U is degenerate along the curve

$$(\frac{\partial p}{\partial V})_T = 0 \tag{6.3}$$

which is usually presented in one of two forms: $p = p(V)$ or/and $T = T(V)$. The critical triple point of the system is the extremum point of these functions.

Note that it is possible to write the isothermal compressibility in terms of the determinant:

$$k = \frac{T}{VC_v det(\eta_{Uij})} \tag{6.4}$$

Remark 6. Determinant of our matrix η_{Uij} is the denominator of the expression (5.2) for the scalar curvature R for such a system. This implies that if $det(\eta_{Uij}) \to 0$, then $R \to \infty$. Therefore, along this curve the Weinhold metric of the thermodynamical phase space changes signature and its curvature is singular. As we will see, in the example of the van der Waals gas, this is also the curve along which phase transition occurs. Thus, this curve determines the boundary of the equilibria region $\mathcal{E}q$ on the constitutive surface Σ_U.

Remark: Speed of sound.

Let ν_{sound}^i and ν_{sound}^a respectively be the speed of sound in terms of isothermal and adiabatic compressibility k and k_S. It is known that $k_S = \frac{C_v}{C_p}k$. So, the speed of sound in a thermodynamical system is given by

$$\nu_{sound}^a = \sqrt{\frac{vC_p det(\eta_{Uij})}{T\rho}} \propto \frac{1}{R}$$

or

$$\nu_{sound}^i = \sqrt{\frac{vC_v det(\eta_{Uij})}{T\rho}} \propto \frac{1}{R}$$

where R is the scalar curvature of the system.

In region where $det(\eta_U) \neq 0$ the inverse of η_{Uij} is given by

$$\eta_U^{ij} = \begin{pmatrix} \frac{C_p}{T} & V\alpha \\ V\alpha & kV \end{pmatrix} \tag{6.5}$$

Let's calculate now the third derivatives of the energy E. We get

$$\eta_{11,_1} = \frac{T}{C_v^2}(1 - (\frac{\partial C_v}{\partial S})_v) \tag{6.6}$$

$$\eta_{11,_2} = -\frac{T}{C_v^2}(\frac{\alpha}{k} + (\frac{\partial C_v}{\partial V})_s) \tag{6.7}$$

$$\eta_{12,_2} = \frac{1}{k^2C_v^2}(-kTC_v(\frac{\partial \alpha}{\partial V})_s + Tk\alpha(\frac{\partial C_v}{\partial V})_s + TC_v\alpha(\frac{\partial k}{\partial V})_s + T\alpha^2) \tag{6.8}$$

$$\eta_{22,_2} = \frac{1}{k^2C_v^2}(2TC_v\alpha(\frac{\partial \alpha}{\partial V})_s - T\alpha^2(\frac{\partial C_v}{\partial V})_s - \frac{T\alpha^3}{k} - \frac{kC_v^2}{V^2}$$

$$-(\frac{C_v^2}{V} + \frac{2TC_v\alpha^2}{k})(\frac{\partial k}{\partial V})_s) \tag{6.9}$$

Now, since $\eta_{11,_2} = \eta_{12,_1}$, where

$$\eta_{12,_1} = -\frac{T}{C_v^2}(\frac{\alpha}{k}(1 - (\frac{\partial C_v}{\partial S})_v) + \frac{C_v}{k}(\frac{\partial \alpha}{\partial S})_v - \frac{C_v\alpha}{k^2}(\frac{\partial k}{\partial S})_v) \tag{6.10}$$

we get the following

Lemma 2. *Identity I.*

$$\left(\frac{\partial C_v}{\partial V}\right)_s + \frac{\alpha}{k}\left(\frac{\partial C_v}{\partial S}\right)_v = \frac{C_v}{k}\left(\frac{\partial \alpha}{\partial S}\right)_v - \frac{C_v \alpha}{k^2}\left(\frac{\partial k}{\partial S}\right)_v \tag{6.11}$$

Similarly, since $\eta_{12,_2} = \eta_{22,_1}$, where

$$\eta_{22,_1} = \frac{1}{k^2 C_v^2}\left(T\alpha^2\left(1 - \left(\frac{\partial C_v}{\partial S}\right)_v + 2TC_v\alpha\left(\frac{\partial \alpha}{\partial S}\right)_v - \frac{2TC_v\alpha^2}{k}\left(\frac{\partial k}{\partial S}\right)_v - \frac{C_v^2}{V}\left(\frac{\partial k}{\partial S}\right)_v\right) \tag{6.12}$$

we have

Lemma 3. *Identity II*

$$k\left(\frac{\partial}{\partial V}\ln\frac{k}{\alpha}\right)_S = \left(\frac{\partial \alpha}{\partial S}\right)_v - \left(\frac{\alpha}{k} + \frac{C_v}{TV\alpha}\right)\left(\frac{\partial k}{\partial S}\right)_v \tag{6.13}$$

Now, for the components of the Ricci Curvature we have

$$R_{11} = \frac{1}{4}\left(\left(\left(\eta_{21,_1}\right)^2 - \eta_{11,_1}\eta_{21,_2}\right)\eta^{11}\eta^{22} + \left(\eta_{21,_1}\eta_{21,_2} - \eta_{11,_1}\eta_{22,_2}\right)\eta^{12}\eta^{22} + \left(\left(\eta_{21,_2}\right)^2 - \eta_{11,_2}\eta_{22,_2}\right)(\eta^{22})^2\right) \tag{6.14}$$

$$R_{12} = R_{21} = \frac{1}{4}\left(\left(\eta_{11,_1}\eta_{21,_2} - \left(\eta_{21,_1}\right)^2\right)\eta^{11}\eta^{12} + \left(\eta_{11,_1}\eta_{22,_2} - \eta_{21,_2}\eta_{11,_2}\right)(\eta^{12})^2 + \left(\eta_{11,_2}\eta_{22,_2} - \left(\eta_{21,_2}\right)^2\right)\eta^{12}\eta^{22}\right) \tag{6.15}$$

$$R_{22} = \frac{1}{4}\left(\left(\eta_{21,_1}\right)^2 - \eta_{22,_1}\eta_{11,_1}\right)(\eta^{11})^2 + \left(\eta_{21,_2}\eta_{11,_2} - \eta_{11,_1}\eta_{22,_2}\right)\eta^{11}\eta^{12} + \left(\left(\eta_{21,_2}\right)^2 - \eta_{12,_1}\eta_{22,_2}\right)\eta^{11}\eta^{22}\right) \tag{6.16}$$

It is easy to show that

$$R_{11}\eta^{11} = R_{22}\eta^{22} \tag{6.17}$$

and so, scalar curvature is given by,

$$R = 2(R_{11}\eta^{11} + R_{12}\eta^{12}) \tag{6.18}$$

After some calculation, we get

$$R_{11} = \frac{T^2}{4C_v^4 det(\eta_{ij})}[HG + \frac{C_v\alpha}{k^2}F(\frac{TV\alpha}{k}F - J)] \tag{6.19}$$

where

$$H = (\frac{\alpha}{k} - \frac{C_v}{V} + \frac{C_p - C_v}{\alpha}(\frac{\partial\alpha}{\partial V})_s - \frac{C_p}{k}(\frac{\partial k}{\partial V})_s + (\frac{\partial C_v}{\partial V})_s) \tag{6.20}$$

$$G = (\frac{\partial C_v}{\partial V})_s + \frac{\alpha}{k}(\frac{\partial C_v}{\partial S})_v \tag{6.21}$$

$$F = k(\frac{\partial}{\partial V}\ln\frac{k}{\alpha})_S \tag{6.22}$$

and

$$J = 1 - (\frac{\partial C_v}{\partial S})_V \tag{6.23}$$

Then,from the $(1,1)$ component of the Ricci Curvature we derive that

$$R_{12} = R_{21} = -\frac{\alpha}{k}R_{11} \tag{6.24}$$

and

$$R_{22} = \frac{C_p}{TVk}R_{11} \tag{6.25}$$

Therefore, Ricci tensor have the form

$$R_{ij} = R_{11}\begin{pmatrix} 1 & -\frac{\alpha}{k} \\ -\frac{\alpha}{k} & \frac{C_p}{TVk} \end{pmatrix} = \frac{C_v}{T}\eta_{ij}R_{11} \tag{6.26}$$

Scalar curvature is equal to

$$R = \frac{2C_v}{T}R_{11} \tag{6.27}$$

and using (6.19) we get the following result,

Theorem 4. *Scalar curvature of a general two-dimensional elementary system is given by*

$$R = \frac{T}{2C_v^3 det(\eta_{ij})}[HG + \frac{C_v\alpha}{k^2}F(\frac{TV\alpha}{k}F - J)] \tag{6.28}$$

where

$$H = (\frac{\alpha}{k} - \frac{C_v}{V} + \frac{C_p - C_v}{\alpha}(\frac{\partial \alpha}{\partial V})_s - \frac{C_p}{k}(\frac{\partial k}{\partial V})_s + (\frac{\partial C_v}{\partial V})_s), \qquad (6.29)$$

$$G = (\frac{\partial C_v}{\partial V})_s + \frac{\alpha}{k}(\frac{\partial C_v}{\partial S})_v, \quad F = k(\frac{\partial}{\partial V}\ln\frac{k}{\alpha})_S \qquad (6.30)$$

and

$$J = 1 - (\frac{\partial C_v}{\partial S})_v \qquad (6.31)$$

7. Case of constant C_v

Here we discuss the class of systems where C_v is constant - class where both the ideal gas and van der Waals gas are included. In this case we can easily get the general form of the constitutive law $U = U(S, V)$, calculations of the previous section simplifies and we will be able to discuss curvature of metric η_U in more details.

Remark 7. Notice that if molar internal energy U is given as a function of volume V and the temperature T, then the Helmholz equation

$$(\frac{\partial U}{\partial V})_T = T^2\frac{\partial}{\partial T}\left(\frac{p}{T}\right)|_V,$$

leads (see [16], Ch. 6) to the formula

$$C_v = C_{v_{ideal}} + \int_\infty^V T\left(\frac{\partial^2 p}{\partial T^2}\right)_V dV.$$

relating the heat capacity of any 2TD-system to one for ideal or vdW gas. From this formula it follows that, for a 2TD-system for which the integral above converges, heat capacity C_v is constant if and only if

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_V = 0,$$

(i.e. when p is the **linear** function of T).

Let us find possible constitutive laws $S = S(T, V)$, $U = U(S, V)$ for which $C_v -$ *const*. Recall that $C_v = T(\frac{\partial S}{\partial T})_V$. Rewrite this as

$$\frac{\partial S}{\partial T} = \frac{C_v}{T},$$

and integrate:

$$S = C_v ln(T) + f(V), \tag{7.1}$$

with arbitrary function $f(V)$.

On the other hand, $T = \frac{\partial U}{\partial S}$. Substituting this in the definition of C_v in the form $\frac{\partial T}{\partial S} = \frac{T}{C_v}$, we get for U equation

$$\frac{\partial^2 U}{\partial S^2} - \frac{1}{C_v}\frac{\partial U}{\partial S} = 0. \tag{7.2}$$

Integrating once we get

$$\frac{\partial U}{\partial S} = \frac{U}{C_v} + g(V),$$

with an arbitrary function $g(V)$. Setting $f = f_1$ and $g = f_2$ and solving this equation we get the fundamental constitutive law in the form

$$U(S,V) = f_1(V)e^{S/C_v} - C_v f_2(V), \tag{7.3}$$

with arbitrary functions $f_i(V)$.

Example 4. Case of the ideal gas is obtained here if we take $f_1 = V^{-\frac{R}{C_v}}$, $f_2 = 0$ since $U = V^{-\frac{R}{C_v}}e^{\frac{S}{C_v}}$ with $U_0 = 0$ and $S_0 = 0$.(see section 9).

Example 5. For the Van der Waals gas we take $f_1 = (V-b)^{-\frac{R}{C_v}}$, $f_2 = \frac{a}{C_v V}$ since $U = (V-b)^{-\frac{R}{C_v}}e^{\frac{S}{C_v}} - \frac{a}{V}$ with $U_0 = 0$ and $S_0 = 0$.(see section 10).

Taking derivatives by both variables and excluding S from these relations we find the following state equation

$$p = -C_v T\frac{f_1'(V)}{f_1(V)} + C_v f_2'(V). \tag{7.4}$$

Calculating derivative of (7.3) and denoting $f_i(V) = f_i$ for i=1,2, we get

$$\left(\frac{\partial U}{\partial S}\right)_v = \frac{f_1}{C_v}e^{\frac{S}{C_v}}, \quad \left(\frac{\partial U}{\partial V}\right)_s = f_1'e^{\frac{S}{C_v}} - C_v f_2', \tag{7.5}$$

$$\eta_{11} = \left(\frac{\partial^2 U}{\partial S^2}\right)_v = \frac{f_1}{C_v^2}e^{\frac{S}{C_v}} \tag{7.6}$$

$$\eta_{12} = \eta_{21} = \left(\frac{\partial^2 U}{\partial S\partial V}\right) = \frac{f_1'}{C_v}e^{\frac{S}{C_v}} \tag{7.7}$$

$$\eta_{22} = (\frac{\partial^2 U}{\partial V^2})_s = f_1'' e^{\frac{S}{C_v}} - C_v f_2'' \tag{7.8}$$

As a result we get the metric η_U in the form

$$\eta_{Uij} = \begin{pmatrix} \frac{f_1}{C_v^2} e^{\frac{S}{C_v}} & \frac{f_1'}{C_v} e^{\frac{S}{C_v}} \\ \frac{f_1'}{C_v} e^{\frac{S}{C_v}} & f_1'' e^{\frac{S}{C_v}} - C_v f_2'' \end{pmatrix} \tag{7.9}$$

with the determinant

$$\det \eta_{ij} = \frac{e^{\frac{2S}{C_v}}}{C_v^2}(f_1 f_1'' - (f_1')^2 - e^{\frac{-S}{C_v}} C_v f_1 f_2'')$$

$$= \frac{e^{\frac{2S}{C_v}}}{C_v^2}(f_1 f_1'' - (f_1')^2) - \frac{e^{\frac{S}{C_v}}}{C_v^2} f_1 f_2'' \tag{7.10}$$

Consider, now, a special case of a constitutive relation (7.9) with the same f_1 and with $f_2 = 0$(ideal gas), and mark this case with 0. For this case

$$\det \eta_{ij,0} = \frac{e^{\frac{2S}{C_v}}}{C_v^2}(f_1 f_1'' - (f_1')^2) \tag{7.11}$$

This determinant is zero if and only if $f_1 f_1'' - (f_1')^2 = 0$, i.e. if $f_1 = c_1 e^{c_2 V}$ with positive constants c_i.

Now we have the important relation

Lemma 4.

$$\det \eta_{ij,real} = \det \eta_{ij,0} - \frac{e^{\frac{S}{C_v}}}{C_v^2} f_1 f_2'' \tag{7.12}$$

Calculate third derivatives of U of the form (6.3):

$$\eta_{11,_1} = \frac{f_1}{C_v^3} e^{\frac{S}{C_v}} = \frac{1}{C_v} \eta_{11} \tag{7.13}$$

$$\eta_{12,_1} = \eta_{21,_1} = \eta_{11,_2} = \frac{f_1'}{C_v^2} e^{\frac{S}{C_v}} = \frac{1}{C_v} \eta_{12} \tag{7.14}$$

$$\eta_{12,_2} = \eta_{21,_2} = \eta_{22,_1} = \frac{f_1''}{C_v} e^{\frac{S}{C_v}} = \frac{1}{C_v} \eta_{22} + f_2'' \tag{7.15}$$

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$$\eta_{22,_2} = f_1''' e^{\frac{S}{C_v}} - C_v f_2''' \tag{7.16}$$

Using these derivatives in formula (6.19) for the component R_{11} of the Ricci tensor we get:

$$R_{11} = \frac{e^{\frac{S}{C_v}} f_1 f_2''}{4 C_v e^{\frac{S}{C_v}} (f_1 f_1'' - (f_1')^2 - e^{\frac{-S}{C_v}} C_v f_1 f_2'')^2} (f_1 f_1'' - (f_1')^2) \tag{7.17}$$

which can be written as

$$R_{11} = \frac{e^{\frac{S}{C_v}} f_1 f_2''}{4 C_v^3} \frac{\det \eta_{ij,_0}}{(\det \eta_{ij,_{real}})^2} \tag{7.18}$$

So, finally we get scalar curvature to be

$$R = \frac{e^{\frac{S}{C_v}} f_1 f_2''}{2 T C_v^2} \frac{\det \eta_{ij,_0}}{(\det \eta_{ij,_{real}})^2} = \frac{T f_1 f_2'' [f_1 f_1'' - (f_1')^2]}{2 [T (f_1 f_1'' - (f_1')^2) - f_1^2 f_2'']^2} \tag{7.19}$$

This leads to the following statement:

Proposition 1. *Let $C_v = const$ and let the internal energy $U(S,V)$ be given by the fundamental constitutive relation*

$$U(S,V) = f_1(V)e^{S/C_v} - C_v f_2(V), \tag{7.20}$$

then the curvature of Weinhold metric is zero in a domain $D \subset R^2$,

$$R(\eta_U)|_D = 0$$

if and only if one of three cases holds:

   (1)
$$f_1 = c_1 e^{c_2 V},$$

     for some positive constants c_i,

   (2)
$$f_2 = AV + B,$$

     with some constants A, B, that includes the case of ideal gas.

   (3)
$$f_1(V) = 0,$$

     degenerate case.

It is interesting to see how the scalar curvature is expressed, in the case $C_v - const$, in terms of isothermal compressibility k. We calculate

$$\eta_{11,_1} = \frac{T}{C_v^2} = \frac{1}{C_v}\eta_{11}, \ \eta_{11,_2} = \eta_{12,1} = -\frac{T\alpha}{C_v^2 k} = \frac{1}{C_v}\eta_{12}, \tag{7.21}$$

$$\eta_{12,_2} = \eta_{22,1} = \frac{1}{k^2 C_v^2}(\alpha^2 T - \frac{C_v^2}{V}(\frac{\partial k}{\partial S})_v) = \frac{1}{T}((\eta_{12})^2 - \frac{T}{Vk^2}(\frac{\partial k}{\partial S})_v), \tag{7.22}$$

$$\eta_{22,_2} = \frac{1}{k^2 C_v^2}(2\frac{C_v^2\alpha}{Vk}(\frac{\partial k}{\partial S})_v - \frac{C_v^2}{V}(\frac{\partial k}{\partial V})_s - \frac{T\alpha^3}{k} - \frac{kC_v^2}{V^2}). \tag{7.23}$$

Moreover (6.15) reduces to the following

Lemma 5. *Identity III*

$$(\frac{\partial \alpha}{\partial k})_v = \frac{\alpha}{k} \tag{7.24}$$

From which we also get that (6.13) becomes

$$\alpha(\frac{\partial}{\partial V}\ln\frac{\alpha}{k})_S = \frac{C_v}{TVk}(\frac{\partial k}{\partial S})_v \tag{7.25}$$

Proposition 2. *Scalar curvature of metric η_U, in the case of a constant C_v, is given by*

$$R = \frac{C_v}{2Tk^2}(\frac{\partial k}{\partial S})_v((\frac{\partial k}{\partial S})_v + \frac{k}{C_v}) = \frac{C_v}{2T}\left(\frac{\partial ln(k)}{\partial S}\Big|_v\right) \times \left(\frac{\partial ln(k)}{\partial S}\Big|_v + \frac{1}{C_v}\right) \tag{7.26}$$

Proof. Since C_v is constant, we can use (6.22) and (7.25) to get

$$F = -\frac{C_v}{TV\alpha}(\frac{\partial k}{\partial S})_v \tag{7.27}$$

Therefore, after some calculation and considering $G = 0$ and $det(\eta_{ij}) = \frac{T}{kVC_v}$, we get (7.26). $\square$

Corollary 1. *Curvature $R(\eta_U)$ is* **negative** *if and only if*

$$-\frac{1}{C_v} < \frac{\partial ln(k)}{\partial S}\Big|_v < 0.$$

8. Ideal Gas

Here we consider the ideal gas, the simplest model example of a TD system with two degrees of freedom. For more detailed discussion of Weinhold metric(s) for ideal gas in different representations we refer to [23]. Except its illustrative interest, ideal gas will serve us as a reference point in the further study of curvature of metric η_E for non-ideal gases.

Internal energy U of the ideal gas as a function of S, V and the mole number N has the form

$$U = U_0 + C_V N \left(\frac{V}{N}\right)^{-\frac{R}{C_v}} e^{\frac{1}{C_V}(\frac{S}{N}-S_0)}, \tag{8.1}$$

with some reference constants U_0, S_0, see [16], Chapter 6. Other equations of state are obtained from (8.1) in a standard way:

$$pV = NRT, \ U = C_V NT, \ TS + \mu N = C_P NT. \tag{8.2}$$

We will take $N = 1$. Then it is known that

$$S = S_0 + C_v \ln U + R \ln V$$

from which we can solve for U obtaining

$$U = U(S, V) = U_0 + C_v V^{-\frac{R}{C_v}} e^{\frac{S-S_0}{C_v}}$$

Weinhold metric for an Ideal Gas is given by (3.14). Setting $S_0 = 0$, we get

$$\eta_{U_{ij}} = \frac{1}{C_v} \begin{pmatrix} T & -p \\ -p & \frac{C_p p}{V} \end{pmatrix} = \frac{R}{C_v} e^{\frac{S}{C_v}} \begin{pmatrix} \frac{1}{R} V^{-\frac{R}{C_v}} & -V^{-\frac{C_p}{C_v}} \\ -V^{-\frac{C_p}{C_v}} & C_p V^{-(1+\frac{C_p}{C_V})} \end{pmatrix}. \tag{8.3}$$

In this case C_v and C_p are positive constants. From (5.5) we get

$$det(\eta) = \frac{p}{V C_v^2}(T C_p - pV) = \frac{pT}{V C_v} = \frac{R}{C_v} e^{2\frac{S}{C_v}} V^{-2(\frac{C_p}{C_v})} > 0 \tag{8.4}$$

which is always positive. Thus, Weinhold metric is **positive definite** on the constitutive surface Σ_U.

Inverse of η_{Uij} is given by

$$\eta_U^{ij} = \begin{pmatrix} \frac{C_p}{T} & \frac{V}{T} \\ \frac{V}{T} & \frac{V}{p} \end{pmatrix} \tag{8.5}$$

Now, (6.6) through (6.9) become

$$\eta_{11,_1} = \frac{T}{C_v^2}, \qquad \eta_{11,_2} = \eta_{12,_1} = \eta_{21,_1} = -\frac{p}{C_v^2} \tag{8.6}$$

$$\eta_{22,_1} = \eta_{12,_2} = \eta_{21,_2} = \frac{p\gamma}{vC_v}, \qquad \eta_{22,_2} = -(\gamma+1)\frac{p\gamma}{v^2} \tag{8.7}$$

where $\gamma = \frac{C_p}{C_v}$.

For the component R_{11} of the Ricci Tensor R_{ij} of ideal gas we get

$$R_{11} = (R - C_p)\frac{C_p}{C_v^4} + (C_p + C_v - R)\frac{C_p}{C_v^4} - \frac{C_p}{C_v^3} = 0. \tag{8.8}$$

Using (6.26), we get the known result (see [23]):

$$R_{ij} = 0 \qquad \forall i, j = 1, 2. \tag{8.9}$$

and, therefore,

$$R(\eta_U) = 0 \tag{8.10}$$

Zero curvature of Weinhold metric (as well as of Ruppeiner metric based on entropy [30]) is positively correlated with the known suggestion to use thermodynamical curvature as the characteristic of interactions on the microscopic level of media description.

9. Van der Waals Gas

Let's consider now a Van der Waals gas whose equation of state is given by

$$(p + \frac{a}{V^2})(V - b) = RT, \tag{9.1}$$

where a and b are positive constants. This equation represents the behavior of real gases more accurately than the ideal gas by introducing two additional positive constants a and b characteristic (of molecule interaction in the gas and of the part of the volume occupied by the molecules correspondingly, see [5]) of the particular gas under consideration.

For the coefficients α and k we get

$$\alpha = \frac{RV^2}{pV^3 - aV + 2ab} = \frac{RV^2(V-b)}{RTV^3 - 2a(V-b)^2} \tag{9.2}$$

and

$$k = \frac{(V-b)V^2}{pV^3 - aV + 2ab} = \frac{V^2(V-b)^2}{RTV^3 - 2a(V-b)^2} \tag{9.3}$$

Therefore the relation between the coefficient of expansion and the isothermal compressibility is given by $\alpha = \frac{R}{(V-b)}k$.

The entropy of VdW gas per one mole $(N = 1)$ is given by,[16],

$$S = R\ln(V-b)(U + \frac{a}{V})^{\frac{C_v}{R}} + S_0. \tag{9.4}$$

The internal energy of Van der Waals gas as a function of S and V is obtained from the last equation, namely

$$U = U_0 + (V-b)^{-\frac{R}{C_v}}e^{\frac{S}{C_v}} - \frac{a}{V} \tag{9.5}$$

Then, the Weinhold metric of this gas is given by

$$\eta_{Uij} = \begin{pmatrix} \frac{T}{C_v} & -\frac{TR}{(V-b)C_v} \\ -\frac{TR}{(V-b)C_v} & (\frac{TR}{(V-b)^2}(1+\frac{R}{C_v}) - \frac{2a}{V^3}) \end{pmatrix} \tag{9.6}$$

$$= \begin{pmatrix} \frac{1}{C_v^2}e^{\frac{S}{C_v}}(V-b)^{-\frac{R}{C_v}} & -\frac{R}{C_v^2}e^{\frac{S}{C_v}}(V-b)^{-(1+\frac{R}{C_v})} \\ -\frac{R}{C_v^2}e^{\frac{S}{C_v}}(V-b)^{-(1+\frac{R}{C_v})} & \frac{R}{C_v^2}e^{\frac{S}{C_v}}(C_v+R)(V-b)^{-(2+\frac{R}{C_v})} - \frac{2a}{V^3} \end{pmatrix}, \tag{9.7}$$

with C_v being constant. In the limit $a \to 0$, $b \to 0$ to the Ideal Gas we get exactly the metric (8.3). The determinant is then given by

$$det(\eta_{ij}) = \frac{RT^2V^3 - 2aT(V-b)^2}{V^3 C_v(V-b)^2} = \frac{T}{V^3(V-b)C_v}(pV^3 - aV + 2ab) \tag{9.8}$$

$$= \frac{1}{C_v^2} \frac{e^{\frac{S}{C_v}}}{(V-b)^{\frac{R}{C_v}}} [\frac{Re^{\frac{S}{C_v}}}{C_v(V-b)^{2+\frac{R}{C_v}}} - \frac{2a}{V^3}] \tag{9.9}$$

which is zero along the curve γ_η

$$S = S(V) = C_v[(2+\frac{R}{C_v}) \ln(V-b) + \ln(\frac{2aC_v}{RV^3})] \tag{9.10}$$

or, when $pV^3 - aV + 2ab = 0$, supposing of course that our system is at non-zero temperature.

The determinant of the metric η_U is positive if entropy is large enough

$$S = S(V) > C_v[(2+\frac{R}{C_v}) \ln(V-b) + \ln(\frac{2aC_v}{RV^3})]$$

and negative if the opposite is true.

The inverse of tensor η_{Uij} is given by

$$\eta_U^{ij} = \begin{pmatrix} (\frac{C_v}{T} + \frac{R^2V^3}{RTV^3 - 2a(V-b)^2}) & \frac{RV^3(V-b)}{RTV^3 - 2a(V-b)^2} \\ \frac{RV^3(V-b)}{RTV^3 - 2a(V-b)^2} & \frac{V^3(V-b)^2}{RTV^3 - 2a(V-b)^2} \end{pmatrix} \tag{9.11}$$

.

Now, we calculate the third derivatives of the energy U. We get

$$\eta_{11,1} = \frac{T}{C_v^2}; \quad \eta_{12,1} = \eta_{21,1} = \eta_{11,2} = -\frac{RT}{(V-b)C_v^2}; \tag{9.12}$$

$$\eta_{12,2} = \eta_{21,2} = \eta_{22,1} = \frac{RT}{C_v(V-b)^2}(1+\frac{R}{C_v}); \quad \eta_{22,2} = \frac{6a}{V^4} - \frac{RT}{(V-b)^3}(1+\frac{R}{C_v})(2+\frac{R}{C_v}) \tag{9.13}$$

Then, the component R_{11} of the Ricci Tensor is given by

$$R_{11} = \frac{aRTV^3(V-b)^2}{2C_v^2(RTV^3 - 2a(V-b)^2)^2} \tag{9.14}$$

From (6.27), we get the scalar curvature $R(\eta_U)$ of the Weinhold metric to be

$$R(\eta_U) = \frac{aRV^3}{C_v(pV^3 - aV + 2ab)^2} \qquad (9.15)$$

The scalar curvature goes to zero as $a \to 0$ or as $V \to \infty$. Since the quantity $\frac{a}{V^2}$ characterizes the attractive interaction within a system, scalar curvature seems to be a measure of the attraction among particles while its dependence on the parameter b is more quantitative then qualitative. On the other hand, as we have seen before if $det(\eta_{ij}) \to 0$ then $R \to \infty$ i.e. **at the curve γ_η of the signature change, scalar curvature R has the singularity inverse quadratic by the distance to the curve**.

Remark 8. It is interesting to note that, combining (7.15) and Example 5 (see Sec. 7), we get

$$\left(\frac{\partial \eta_{22}}{\partial S}\right)_v = \frac{\eta_{22}}{C_v} + \frac{2a}{C_v V^3}, \qquad (9.16)$$

.

So, it seems reasonable to consider the quantity

$$\left(\frac{\partial \eta_{22}}{\partial S}\right)_v - \frac{\eta_{22}}{C_v} = \delta(S, V) \qquad (9.17)$$

as a measure of non-interaction of the system as long as C_v is constant. In the case of the Ideal Gas, $\delta(S, V) = 0$. For the Van der Waals Gas, $\delta(S, V) = \frac{2a}{C_v V^3}$. notice that the parameter b is not present in $\delta(S, V)$. In the limit where $a \to 0$, with a fixed volume, Van der Waals gas becomes Ideal even if $b \neq 0$.

Let's now look at what happens when $R \to \infty$. As we discussed earlier, when R goes to infinity, the system is described by a *degeneracy curves* γ_η on which phase transition seems to happen. Now, since the critical point is obtained whenever both $\left(\frac{\partial p}{\partial v}\right)_T = 0$ and $\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$ are satisfied, it is evident that, the idea of phase transition is given by the degeneracy of the Weinhold metric. What follows are the derivations of the critical point for the Van der Waals gas through the zero-determinant of the metric matrix η_{Uij}. Indeed, considering the denominator of R being zero, we obtain:

$$pV^3 - aV + 2ab = 0 \qquad (9.18)$$

Then, we get the curve γ_η in the p-V plane

$$p(V) = (V - 2b)\frac{a}{V^3} \tag{9.19}$$

Taking derivative with respect to V, we get

$$\frac{dp}{dV} = (3b - V)\frac{2a}{V^4} \tag{9.20}$$

which is zero when

$$V_c = V = 3b \tag{9.21}$$

This is exactly the critical value of the volume for the van der Waals gas. Now, substituting this value back into the equation (9.22), we get the critical value for pressure

$$p_c = p = \frac{a}{27b^2} \tag{9.22}$$

Naturally, if we consider the denominator of the scalar curvature with T and V in it and set it to zero we get the degeneracy curve γ_η in the T-V plane

$$T(V) = \frac{2a(V - b)^2}{RV^3} \tag{9.23}$$

and since $V_c = 3b$ then we get,

$$T_c = \frac{8a}{27bR} \tag{9.24}$$

Consider, now, $p_r = \frac{p}{p_c}$, $V_r = \frac{V}{V_c}$ and $T_r = \frac{T}{T_c}$.
Then

$$p_r = \frac{3V_r - 2}{V_r^3} \tag{9.25}$$

and

$$T_r = \frac{(3V_r - 1)^2}{4V_r^3} \tag{9.26}$$

Naturally, the two curves intersect at the critical point.

Solving (9.21) for V_r, we have the three roots of volume in terms of pressure, namely

$$V_r^1(p) = \frac{((3)^{\frac{1}{2}}sign(p)\cos(h(p)) - \sin(h(p))}{p^{\frac{1}{2}}} \tag{9.27}$$

$$V_r^2(p) = -\frac{((3)^{\frac{1}{2}}sign(p)\cos(h(p)) - \sin(h(p))}{p^{\frac{1}{2}}} \tag{9.28}$$

$$V_r^3(p) = \frac{2h(p)}{p^{\frac{1}{2}}} \tag{9.29}$$

where $h(p) = \frac{\arcsin(p^{\frac{1}{2}})}{3}$.

Now, solving (9.26) for V_r, we similarly get the roots of volume in terms of temperature, namely

$$V_r^1(T) = ((3f(T))^{\frac{1}{2}}\cos(\frac{g(T)}{3})\frac{1}{4|T|} + (f(T)^{\frac{1}{2}}\sin(\frac{g(T)}{3})\frac{1}{4T} + \frac{3}{4T}) \tag{9.30}$$

$$V_r^2(T) = -((3f(T))^{\frac{1}{2}}\cos(\frac{g(T)}{3})\frac{1}{4|T|} + (f(T)^{\frac{1}{2}}\sin(\frac{g(T)}{3})\frac{1}{4T} + \frac{3}{4T}) \tag{9.31}$$

$$V_r^3(T) = \frac{3}{4T} - (f(T)^{\frac{1}{2}}\sin(\frac{g(T)}{3})\frac{1}{2T}) \tag{9.32}$$

where $f(T) = 9 - 8T$ and

$$g(T) = \arctan(\frac{(8T^2 - 36T + 27)(-f(T))^{\frac{3}{2}}}{8(f(T)^{\frac{3}{2}})(T^3(T-1))^{\frac{1}{2}}}) \tag{9.33}$$

Therefore, substituting these last three solutions in (9.28), we get

$$p_r^i(T) = \frac{3V_r^i(T) - 2}{(V_r^i(T))^3} \tag{9.34}$$

with $i = 1, 2, 3$.

In particular, for $i = 3$, we get the interesting *coexistence* curve(Fig.1),

Considering $i = 1, 2$, instead, we get (Fig.2,3)

Now, differentiating (9.28) and (9.29), then we get

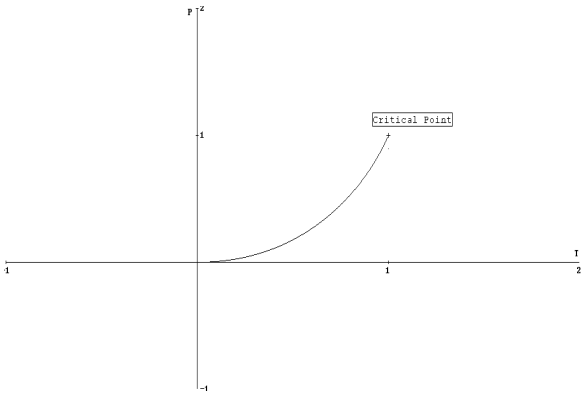$$\frac{dp_r}{dT_r} = \frac{8}{3V_r - 1} \tag{9.35}$$

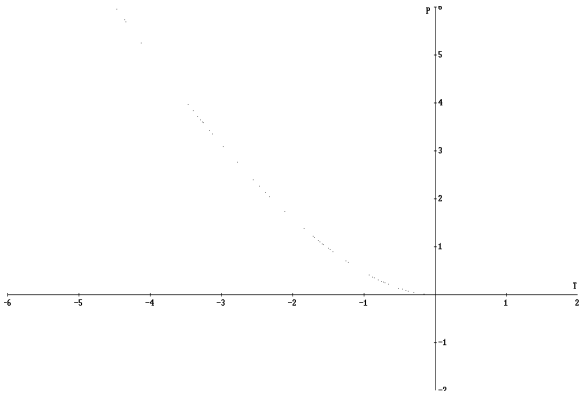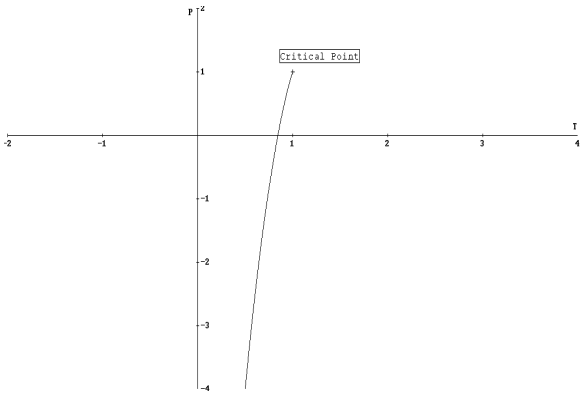FIGURE 1. Solution 1: Coexistence curve

FIGURE 2. Solution 2

FIGURE 3. Solution 3

The important conclusion we gain by looking at the Van der Waals gas is that the singular locus $Sing(\eta_U)$ of Weinhold metric carries important information on the critical behavior of the one component system. In particular, along the curve $Sing(\eta_U) = \gamma_\eta$ phase transitions happens and exterma of coordinate functions along this curve corresponds to the critical points of the system.

10. BERTHELOT'S GAS

Consider Berthelot's gas (see [16], Chapter 6) whose conventional equation of state is

$$(p + \frac{a}{TV^2})(V - b) = RT, \tag{10.1}$$

where a and b are positive constants having the same meaning as for the Van der Waals gas. For this gas, C_v is not constant. In particular,

$$(C_v)_{Bert} = (C_v)_{ideal} + \frac{2a}{VT^2} \tag{10.2}$$

Moreover,

$$k = \frac{TV^2(V - b)^2}{RT^2V^3 - 2a(V - b)^2} = \frac{TV^2(V - b)}{pTV^3 - aV + 2ab} \tag{10.3}$$

and

$$\alpha = \frac{(V - b)(RT^2V^2 + a(V - b))}{T(RT^2V^3 - 2a(V - b)^2)} = \frac{(V - b)(pTV^2 + 2a)}{T(pTV^3 - aV + 2ab)} \tag{10.4}$$

Therefore the relation between k and α is given by

$$\frac{\alpha}{k} = \frac{R}{V - b} + \frac{a}{T^2V^2} \tag{10.5}$$

It is also interesting to look at the rates of change of the heat capacity at constant volume. In particular, denoting $(C_v)_{Bert}$ by C_v and considering (10.2), we get

$$(\frac{\partial C_v}{\partial S})_v = -\frac{4a}{C_vVT^2} \tag{10.6}$$

and

$$(\frac{\partial C_v}{\partial V})_s = \frac{2a}{C_v V T^2}(\frac{2a}{T^2 V^2} + \frac{2R}{(V-b)} - \frac{C_v}{V}) \qquad (10.7)$$

The Weinhold metric η_{ij} of the Berthelot's gas given by

$$\eta_{Uij} = \begin{pmatrix} \frac{T}{C_v} & -\frac{1}{C_v}(\frac{RT}{(V-b)} + \frac{a}{TV^2}) \\ -\frac{1}{C_v}(\frac{RT}{(V-b)} + \frac{a}{TV^2}) & \frac{RT^2V^3 - 2a(V-b)^2}{TV^3(V-b)^2} + \frac{T}{C_v}(\frac{R}{(V-b)} + \frac{a}{T^2V^2})^2 \end{pmatrix} \qquad (10.8)$$

The determinant is then given by

$$\det(\eta_{Uij}) = \frac{RT^2V^3 - 2a(V-b)^2}{C_v V^3 (V-b)^2} \qquad (10.9)$$

If we set the determinant of η_{Uij} equal zero we get the singular locus $Sing(\eta_U)$ of the Bertellot gas

$$RT^2V^3 - 2a(V-b)^2 = 2p^2V^3(V-b)^2 - aR(V-2b)^2 = 0 \qquad (10.10)$$

and solving the first equation for T we get

$$T(V) = \pm\frac{(V-b)}{V}(\frac{2a}{RV})^{\frac{1}{2}} \qquad (10.11)$$

Taking derivative with respect to V, we get

$$\frac{dT}{dV} = \pm\frac{1}{2V}(\frac{2a}{RV})^{\frac{1}{2}}(2 - \frac{3(V-b)}{V}) \qquad (10.12)$$

which is zero when

$$V_c = V = 3b \qquad (10.13)$$

considering $a \neq 0$. This implies that

$$T_c = \pm(\frac{8a}{27Rb})^{\frac{1}{2}} \qquad (10.14)$$

and, therefore, since $p(V) = \frac{aV - 2ab}{TV^3}$ whenever $\det(\eta_{Uij}) = 0$, we have

$$p_c = \pm(\frac{aR}{216b^3})^{\frac{1}{2}} \qquad (10.15)$$

We could normalize both p and T as function of V. Then

$$p_r^2 = \frac{4(3V_r - 2)^2}{V_r^3(3V_r - 1)} \tag{10.16}$$

and

$$T_r^2 = \frac{3V_r - 1}{4V_r^3} \tag{10.17}$$

Let's calculate the inverse matrix. We have

$$\eta_U^{ij} = \begin{pmatrix} \frac{C_v}{T} + \frac{RV(RT^2V^2+a(V-b))}{T(RT^2V^3-2a(V-b)^2)} + \frac{a(V-b)(RT^2V^2+a(V-b))}{VT^3(RT^2V^3-2a(V-b)^2)} & \frac{V(V-b)(RT^2V^2+a(V-b))}{T(RT^2V^3-2a(V-b)^2)} \\ \frac{V(V-b)(RT^2V^2+a(V-b))}{T(RT^2V^3-2a(V-b)^2)} & \frac{TV^3(V-b)^2}{RT^2V^3-2a(V-b)^2} \end{pmatrix} \tag{10.18}$$

It is convenient, now, to calculate the third derivatives without grouping, in particular,

$$\eta_{11,_1} = \frac{T}{C_v^2} + \frac{4a}{VTC_v^3} \tag{10.19}$$

$$\eta_{12,_1} = \eta_{21,_1} = \eta_{11,_2} = -\frac{R}{(V-b)}\eta_{11,_1} + \frac{a}{C_v^2TV^2}(1 + (\frac{\partial C_v}{\partial S})_v) \tag{10.20}$$

$$\eta_{12,_2} = \eta_{21,_2} = \eta_{22,_1} = \frac{R^2}{(V-b)^2}\eta_{11,_1} - \frac{2aR}{C_v^2TV^2(V-b)}(1 + (\frac{\partial C_v}{\partial S})_v) + \frac{RT}{C_v(V-b)^2}$$

$$+\frac{a}{C_vTV^3}[\frac{4a^2}{C_v^2T^4V^2} - \frac{3a}{C_vVT^2} + 2] \tag{10.21}$$

$$\eta_{22,_2} = -\frac{R^3}{(V-b)^3}\eta_{11,_1} + \frac{\alpha}{k}[\frac{12a^2R}{T^3V^3C_v^3(V-b)} + \frac{7aR}{TV^2C_v^2(V-b)} + \frac{2aR}{TC_v^2} - \frac{6a}{C_vTV^3} - \frac{3RT}{C_v(V-b)^2}]$$

$$-\frac{2RT}{(V-b)^2}[\frac{3aR}{T^2V^2C_v^2} - \frac{1}{(V-b)}] - \frac{a}{TV^4}[\frac{4a^3}{C_v^3T^6V^3} - \frac{5a^2}{C_v^2T^4V^2} + 6] \tag{10.22}$$

Then, from (6.27), we get the scalar curvature to be

$$R(\eta_U) = 2a\frac{(T^4V^4RC_vP(C_v,V) + T^2V^3RaQ(C_v,V) + a^2W(C_v,V))}{C_v^3T^3V(RT^2V^3 - 2a(V-b)^2)^2}, \tag{10.23}$$

where

$$P(C_v, V) = (2C_v - R)V^2 - 3C_v bV + C_v b^2$$

$$Q(C_v, V) = -RV^5 + 3RbV^4 - 3Rb^2 V^3 + (Rb^3 + C_v + R)V^2 - b(b - 2V)(R + C_v)$$

and

$$W(C_v, V) = -RV^7 + 4RbV^6 - 6Rb^2 V^5 + (2C_v + R + 4Rb^3)V^4 - (8C_v + 3R + Rb^3)bV^3 + (12C_v + 3R)b^2 V^2 -$$

$$-(8C_v + R)b^3 V + 2C_v b^4$$

Notice that, as for VdW gas, as a goes to zero then scalar curvature R goes to zero as well, while it is not true in the case of b being zero.

11. GEODESIC EQUATIONS

We found the Christoffel coefficients for a general 2-dimensional thermodynamical phase space to be

$$\Gamma_{ij}^k = \frac{1}{2} \sum_m \eta_{ij,m} \eta^{km} \tag{11.1}$$

Now, the geodesic equations in a general form are given by

$$\frac{d^2 x^k}{dt^2} + \Gamma_{ij}^k \frac{dx^i}{dt} \frac{dx^j}{dt} = 0 \tag{11.2}$$

For our case in which $E = U(S, V)$, the geodesic equations are of the form

$$\frac{d^2 S}{dt^2} + \Gamma_{11}^1 \left(\frac{dS}{dt}\right)^2 + 2\Gamma_{12}^1 \frac{dS}{dt} \frac{dV}{dt} + \Gamma_{22}^1 \left(\frac{dV}{dt}\right)^2 = 0 \tag{11.3}$$

$$\frac{d^2 V}{dt^2} + \Gamma_{11}^2 \left(\frac{dS}{dt}\right)^2 + 2\Gamma_{12}^2 \frac{dS}{dt} \frac{dV}{dt} + \Gamma_{22}^2 \left(\frac{dV}{dt}\right)^2 = 0 \tag{11.4}$$

Let's look at the Christoffel coefficients in more details.

$$\Gamma_{11}^1 = \frac{1}{2}(\eta_{11,1} \eta^{11} + \eta_{11,2} \eta^{12}) \qquad \Gamma_{11}^2 = \frac{1}{2}(\eta_{11,1} \eta^{21} + \eta_{11,2} \eta^{22}) \tag{11.5}$$

$$\Gamma^1_{12} = \Gamma^1_{21} = \frac{1}{2}(\eta_{12,1}\eta^{11} + \eta_{12,2}\eta^{12}) \qquad \Gamma^2_{12} = \Gamma^2_{21} = \frac{1}{2}(\eta_{12,1}\eta^{21} + \eta_{12,2}\eta^{22}) \qquad (11.6)$$

$$\Gamma^1_{22} = \frac{1}{2}(\eta_{22,1}\eta^{11} + \eta_{22,2}\eta^{12}) \qquad \Gamma^2_{22} = \frac{1}{2}(\eta_{22,1}\eta^{21} + \eta_{22,2}\eta^{22}) \qquad (11.7)$$

Considering the following relations:

$$F = k\left(\frac{\partial}{\partial V}\ln\frac{k}{\alpha}\right)_S \qquad (11.8)$$

$$J = 1 - \left(\frac{\partial C_v}{\partial S}\right)_V \qquad (11.9)$$

$$D = \frac{\alpha}{k} + \left(\frac{\partial C_v}{\partial V}\right)_s \qquad (11.10)$$

and

$$B = \frac{\alpha}{V} + \left(\frac{\partial\alpha}{\partial V}\right)_s \qquad (11.11)$$

then, we can calculate the coefficients explicitly,

$$\Gamma^1_{11} = \frac{1}{2}\left[\frac{C_p}{C_v^2}J - \frac{TV\alpha}{C_v^2}D\right] \qquad (11.12)$$

$$\Gamma^1_{12} = \Gamma^1_{21} = -\frac{1}{2}\left[\frac{1}{C_v}D + \frac{TV\alpha^2}{k^2C_v}F\right] \qquad (11.13)$$

$$\Gamma^1_{22} = \frac{1}{2}\left[\frac{\alpha}{kC_v}D - \frac{TV\alpha^3}{k^3C_v}F - \frac{1}{k}B\right] \qquad (11.14)$$

$$\Gamma^2_{11} = \frac{1}{2}\left[\frac{TV\alpha}{C_v^2}J - \frac{TVk}{C_v^2}D\right] \qquad (11.15)$$

$$\Gamma^2_{12} = \Gamma^2_{21} = \frac{1}{2}\left[\frac{TV\alpha}{kC_v}F\right] \qquad (11.16)$$

$$\Gamma^2_{22} = -\frac{1}{2}\left[\frac{C_p}{kC_v}F + \frac{1}{\alpha}B\right] \qquad (11.17)$$

Therefore we have the following proposition:

Proposition 3. *The geodesic equations for a general two dimensional thermodynamical system are given by*

$$\frac{d^2S}{dt^2}+\frac{1}{2}[\frac{C_p}{C_v^2}J-\frac{TV\alpha}{C_v^2}D](\frac{dS}{dt})^2-[\frac{1}{C_v}D+\frac{TV\alpha^2}{k^2C_v}F]\frac{dS}{dt}\frac{dV}{dt}+\frac{1}{2}[\frac{\alpha}{kC_v}D-\frac{TV\alpha^3}{k^3C_v}F-\frac{1}{k}B](\frac{dV}{dt})^2=0$$
$$(11.18)$$

$$\frac{d^2V}{dt^2}+\frac{1}{2}[\frac{TV\alpha}{C_v^2}J-\frac{TVk}{C_v^2}D](\frac{dS}{dt})^2+[\frac{TV\alpha}{kC_v}F]\frac{dS}{dt}\frac{dV}{dt}-\frac{1}{2}[\frac{C_p}{kC_v}F+\frac{1}{\alpha}B](\frac{dV}{dt})^2=0 \quad (11.19)$$

In the case in which C_v is constant, then B and F are the same while the other relations become

$$G = 0 \tag{11.20}$$

$$J = 1 \tag{11.21}$$

$$D = \frac{\alpha}{k} \tag{11.22}$$

So, now, our Christoffel's coefficients become

$$\Gamma_{11}^1 = \frac{1}{2C_v} \tag{11.23}$$

$$\Gamma_{12}^1 = \Gamma_{21}^1 = -\frac{1}{2}[\frac{\alpha}{kC_v}+\frac{TV\alpha^2}{k^2C_v}F] \tag{11.24}$$

$$\Gamma_{22}^1 = \frac{1}{2}[\frac{\alpha^2}{k^2C_v}-\frac{TV\alpha^3}{k^3C_v}F-\frac{1}{k}B] \tag{11.25}$$

$$\Gamma_{11}^2 = 0 \tag{11.26}$$

$$\Gamma_{12}^2 = \Gamma_{21}^2 = \frac{1}{2}[\frac{TV\alpha}{kC_v}F] \tag{11.27}$$

$$\Gamma_{22}^2 = -\frac{1}{2}[\frac{C_p}{kC_v}F+\frac{1}{\alpha}B] \tag{11.28}$$

So, finally, our geodesic equation with C_v constant are given by

Lemma 6.

$$\frac{d^2S}{dt^2} + \frac{1}{2C_v}(\frac{dS}{dt})^2 - [\frac{\alpha}{kC_v} + \frac{TV\alpha^2}{k^2C_v}F]\frac{dS}{dt}\frac{dV}{dt} + \frac{1}{2}[\frac{\alpha^2}{k^2C_v} - \frac{TV\alpha^3}{k^3C_v}F - \frac{1}{k}B](\frac{dV}{dt})^2 = 0$$
(11.29)

$$\frac{d^2V}{dt^2} + [\frac{TV\alpha}{kC_v}F]\frac{dS}{dt}\frac{dV}{dt} - \frac{1}{2}[\frac{C_p}{kC_v}F + \frac{1}{\alpha}B](\frac{dV}{dt})^2 = 0$$
(11.30)

12. Conclusion

In this work we have studied the scalar (Gauss) curvature of Weinhold metric for a thermodynamical systems with two thermodynamical degrees of freedom. We get criteria for the positivity, nullity and negativity of scalar curvature in terms of *Hessian surface* of the thermodynamical potential, found scalar curvature for a general thermodynamical systems with two thermodynamical degrees of freedom. We have studied relation of the signature change of Weinhold metric and the scalar curvature to the curves of phase transition of these systems. As examples we have considered the systems with the heat capacity C_v constant, in particular the Ideal and Van der Waals gases, and the Berthelot gas. Results obtained here suggest a kind of duality relation between the constitutive surface of a 2D thermodynamical system in the Gibbs space (Space with coordinates (U, S, V) in the case of internal energy) and its Hessian surface. Relations between the convexity properties of both surfaces, curvature and signature of thermodynamical metric, extremal properties of corresponding thermodynamical potential and the phase transitions in the thermodynamical system present interesting and, in our opinion, highly promising direction of the future work.

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